PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2001-048641**
(43)Date of publication of application : **20.02.2001**

(51)Int.Cl. **C04B 35/46**
H01L 41/187

(21)Application number : **11-222177**
(22)Date of filing : **05.08.1999**

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(54) PIEZOELECTRIC PORCELAIN COMPOSITION

(57)Abstract:
PROBLEM TO BE SOLVED: To produce a piezoelectric porcelain composition which contains no lead and has a high mechanical quality factor by using, as constituent atoms or atomic groups of the composition, Bi, Na, TiO3 and LaFeO3 in specified compositional ratios, respectively.
SOLUTION: This piezoelectric porcelain composition has a composition represented by the general formula (1-x)(Bi0.5Na0.5)TiO3-xLaFeO3 (wherein 0<x≤0.3) and is produced by using Bi2O3, Na2CO3, TiO2, La2O3 and Fe2O3, each having high chemical purity, as raw materials of the main constituents. The production process, for example, comprises: blending the above raw materials stoichiometrically with respect to the general formula to obtain a blend; mixing the blend in ethanol for 20 hr; maintaining the mixed material at 800°C for 1 hr to calcine the mixed material; thereafter crushing the calcined material over a 10 hr period; granulating the crushed material with polyvinyl alcohol as a binder into granules; subjecting the granules to press forming under 1 ton/cm2 pressure into a disklike body having a 20 mm diameter and a 1 mm thickness; sintering the disklike body at 1,100-1,200°C while maintaining the body at that temperature for 2 hr, to form a disklike sintered body; polishing the disklike sintered body so as to form its upper and lower parallel planes to each other; placing two silver electrodes on the upper and lower planes of the sintered body, respectively; and applying a DC electric field having a 4 kV/mm intensity to between the two silver electrodes in silicone oil maintained at 100°C to effect a polarization in the thickness direction in the sintered body. Thus, the objective piezoelectric porcelain composition can be produced and applied to various piezoelectric devices such as filter and vibrator.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（Ａ）　(11)特許出願公開番号
特開2001－48641
（P2001－48641A）
(43)公開日　平成13年２月20日(2001.2.20)

(51)Int.Cl.'	識別記号	Ｆ Ｉ		ﾃｰﾏｺｰﾄﾞ(参考)
Ｃ０４Ｂ　35/46		Ｃ０４Ｂ　35/46	Ｊ	４Ｇ０３１
Ｈ０１Ｌ　41/187		Ｈ０１Ｌ　41/18	１０１Ｊ	

審査請求　未請求　請求項の数１　ＯＬ　（全４頁）

(21)出願番号　特願平11－222177

(22)出願日　平成11年８月５日(1999.8.5)

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Ｆターム(参考)　4G031 AA01 AA09 AA11 AA21 AA35
BA10

(54)【発明の名称】　圧電磁器組成物

(57)【要約】
【課題】　無鉛で、高い機械的品質係数を有する圧電磁器組成物を提供する。
【解決手段】　一般式（１－Ｘ）（Ｂｉ０．５Ｎａ０．５）ＴｉＯ３－ＸＬａＦｅＯ３において、Ｘを０＜Ｘ≦０．３の範囲とする。

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【特許請求の範囲】

【請求項1】　一般式（1－X）（$Bi_{0.5}Na_{0.5}$）TiO_3－$XLaFeO_3$で表され、Xが0＜X≦0．3の範囲であることを特徴とする圧電磁器組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、波動デバイス、センサー、アクチュエーター等に用いられる圧電磁器組成物に関する。

【0002】

【従来の技術】従来、この種の圧電磁器組成物としては、二成分で構成されるPZT（$PbTiO_3$－$PbZrO_3$）系磁器や三成分で構成されるPCM［$PbTiO_3$－$PbZrO_3$－$Pb(Mg_{0.5}Nb_{0.5})TiO_3$］系磁器が主に用いられてきた。その理由としては、上記の組成物が大きな圧電性を示すことはもちろんであるが、それとともに、その用途がセンサー、アクチュエーター、フィルター等多種にわたり、各用途に要求される特性も様々であるのに対し、上記組成系では、各成分量の割合を調整することにより、要求に対応した特性に適宜に操作できるからである。

【0003】しかし、これらの組成物は、いずれも鉛を主成分とするもので、原料比で酸化鉛として60wt％以上も含まれている。酸化鉛は、低温でも揮発性が高く、仮焼、焼結等の製造時に揮発したり、また、産業廃棄物中から溶出することも考えられる。しかし、これらを予防する対策をするには、設備設置のため膨大な費用を投じなければならない。そこで、無鉛で、大きな圧電特性を示す材料が要望されている。

【0004】また、既存の無鉛圧電磁器組成物、一般式（$Bi_{0.5}Na_{0.5}$）TiO_3は、機械的品質係数の値が低く、高い機械的品質係数が必要とされるフィルター、振動子等の用途に適用させることは困難であった。

【0005】

【発明が解決しようとする課題】本発明は、上記の課題を解決し、無鉛で、高い機械的品質係数を有する圧電磁

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器組成物を提供することにある。

【0006】

【課題を解決するための手段】本発明は、一般式（1－X）（$Bi_{0.5}Na_{0.5}$）TiO_3－$XLaFeO_3$で表され、Xが0＜X≦0．3の範囲であることを特徴とする圧電磁器組成物である。

【0007】

【発明の実施の形態】主成分原料として、化学的に高純度であるBi_2O_3、Na_2CO_3、TiO_2、La_2O_3、Fe_2O_3を用いた。これらを一般式（1－X）（$Bi_{0.5}Na_{0.5}$）TiO_3－$XLaFeO_3$（0≦X≦0．4）に対し化学量論的に配合し、ボールミルによりエタノール中で20時間混合した。これを800℃で1時間保持して仮焼し、次に、10時間粉砕を行った。バインダーとしてポリビニルアルコールを用い造粒し、圧力1ton／cm^2で直径20mm、厚さ1mmの円板状に加圧成形した。焼成は、温度1100～1200℃で2時間保持して行った。

【0008】この焼結体を平行平面に研磨し、その上下面に銀電極を設け、100℃のシリコーンオイル中で直流電界4kV／mmを電極間に加え、厚み方向に分極した。

【0009】そして、これらの試料について圧電、誘電特性の測定を行った。圧電特性は、LFインピーダンスアナライザーを用い、共振－反共振法により電気機械結合係数k_{33}、k_p、k_t、機械的品質係数Qmを算出し、評価した。また、誘電特性は、LCRメータを用いて周波数1MHzで測定を行い、比誘電率$\varepsilon_{33}^t/\varepsilon_0$で評価した。

【0010】表1に、（1－X）（$Bi_{0.5}Na_{0.5}$）TiO_3－$XLaFeO_3$において、0≦X≦0．4の範囲におけるk_{33}、k_p、k_t、Qm、及び$\varepsilon_{33}^t/\varepsilon_0$を示す。なお、X＝0．4での空白は、圧電性が確認できなかったことを示している。また、図1に、0≦X≦0．35の範囲のk_{33}、k_p、k_tを示す。

【0011】

【表1】

試料No.	X	k_{33} (%)	kp (%)	kt (%)	Qm	$\varepsilon_{33}^{T}/\varepsilon_{0}$
1	0	32.3	19.0	37.2	243	285
2	0.05	32.7	21.4	38.2	352	406
3	0.1	34.1	23.4	40.3	413	513
4	0.15	37.2	28.0	41.1	472	602
5	0.2	37.1	26.5	40.5	461	541
6	0.25	36.0	24.1	40.3	432	462
7	0.3	35.6	21.8	38.2	418	395
8	0.35	17.2	9.8	18.3	287	276
9	0.4	-	-	-	-	243

【００１２】表１によれば、Ｑｍは、Ｘ＝０．１５で最大値４７２が得られており、（$Bi_{0.5}Na_{0.5}$）TiO_3に対し、Ｑｍが改善したことがわかる。しかし、Ｘ＝０、３＜Ｘの範囲では、Ｑｍが３００以下と非常に小さく、実用化は難しいことがわかる。

【００１３】また、図１から、０＜Ｘ≦０．３の範囲では、k_{33}、ｋｐ、ｋｔは、減少していないのに対し、３＜Ｘでは、急激に低下している。よって、０＜Ｘ≦０．３の範囲が実用に適していると考えられる。

【００１４】以上より、（$Bi_{0.5}Na_{0.5}$）TiO_3に$LaFeO_3$を３０ｍｏｌ％まで固溶させることにより、（$Bi_{0.5}Na_{0.5}$）TiO_3のk_{33}、ｋｐ、ｋｔを劣化させることなく、Ｑｍを向上させることができ、これにより、フィルター、振動子等の用途へ＊の適用が可能となる。

【００１５】

【発明の効果】以上説明したように、本発明によれば、無鉛で、高い機械的品質係数を有する圧電磁器組成物を提供することができた。

【図面の簡単な説明】

【図１】一般式（１－Ｘ）（$Bi_{0.5}Na_{0.5}$）TiO_3－$XLaFeO_3$における０≦Ｘ≦０．３５の範囲のk_{33}、ｋｐ、ｋｔを示す図。

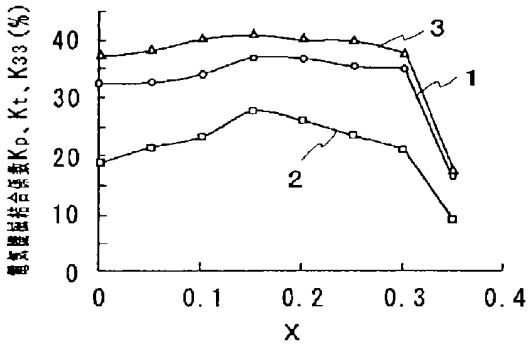
【符号の説明】

１　k_{33}

２　ｋｐ

３　ｋｔ

【図１】



CLAIMS

[Claim(s)]

[Claim 1] The piezoelectric-ceramics constituent which is expressed with general formula (1-X) (Bi0.5Na0.5) TiO3-XLaFeO3, and is characterized by the range of X being 0< X<=0.3.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
['The technical field to which invention belongs] this invention relates to the piezoelectric-ceramics constituent used for a wave-motion device, a sensor, an actuator, etc.
[0002]
[Description of the Prior Art] Conventionally, the PCM[PbTiO3-PbZrO3-Pb(Mg0.5Nb0.5) TiO3] system porcelain which consists of the PZT (PbTiO3-PbZrO3) system porcelain and three components which consist of two components as this kind of a piezoelectric-ceramics constituent has mainly been used. It is because it can be suitably operated in the property corresponding to the demand when the use covers varieties, such as a sensor, an actuator, and a filter, and adjusts the rate of each amount of components by the above-mentioned composition system to properties required of each use being various with it, although piezoelectric [as the reason / with the above-mentioned big constituent] is shown of course.
[0003] However, each of these constituents makes lead a principal component, and is contained more than 60wt% as a lead oxide by the raw material ratio. It volatilizes at the time of manufacture of temporary quenching, sintering, etc., and it is also considered that volatility of a lead oxide is high also at low temperature, and it is eluted out of industrial waste. However, in order to take the measures which prevent these, you have to invest a huge amount of costs for facility installation. Then, the material which shows a piezo-electric unleaded and big property is demanded.
[0004] Moreover, the existing unleaded piezoelectric-ceramics constituent and the general formula (Bi0.5Na0.5) TiO3 had the low value of a mechanical quality factor, and it was difficult to have made it apply to the use of the filter for which a high mechanical quality factor is needed, vibrator, etc.
[0005]
[Problem(s) to be Solved by the Invention] this invention solves the above-mentioned technical problem, and is to offer the piezoelectric-ceramics constituent which has a unleaded and high mechanical quality factor.
[0006]
[Means for Solving the Problem] this invention is a piezoelectric-ceramics constituent which is expressed with general formula (1-X) (Bi0.5Na0.5) TiO3-XLaFeO3, and is characterized by the range of X being 0< X<=0.3.
[0007]
[Embodiments of the Invention] As a principal component raw material, Bi 2O3 which is a high grade chemically, Na2CO3, TiO2 and La 2O3, and Fe2O3 were used. These were blended in stoichiometry to general formula (1-X) (Bi0.5Na0.5) TiO3-XLaFeO3 (0<=X<=0.4), and it mixed in ethanol with the ball mill for 20 hours. At 800 degrees C, this was held for 1 hour, and carried out temporary quenching, next trituration was performed for 10 hours. It corned using polyvinyl alcohol as a binder, and pressing was carried out to disc-like [with a diameter / of 20mm /, and a thickness of 1mm] by pressure 1 ton/cm2. At the temperature of 1100-1200 degrees C, baking was held for 2 hours and performed.
[0008] This sintered compact was ground at the parallel flat surface, the silver electrode was prepared in the vertical side, 4kV [/mm] direct-current electric field were added to inter-electrode in the 100-degree C silicone oil, and it polarized in the thickness direction.
[0009] And measurement of piezo-electricity and dielectric characteristics was performed about these samples. Using LF impedance analyzer, the piezo-electric property computed electromechanical coupling coefficients k33, kp, and kt and the mechanical quality factor Qm by the resonance-antiresonating method, and was evaluated. Moreover, dielectric characteristics measured on the frequency of 1MHz using the LCR meter, and specific-inductive-capacity epsilon33 t/epsilon 0 estimated them.
[0010] In TiO(Bi(1-X)0.5Na0.5)3-XLaFeO3, k33, kp, kt and Qm in the range, and epsilon33 t/epsilon 0 of 0<=X<=0.4 are shown in Table 1. In addition, the null of X= 0.4 shows that it has not checked piezoelectric. Moreover, k33, kp, and kt of the range of 0<=X<=0.35 are shown in drawing 1 .
[0011]
[Table 1]

試料 No.	X	k_{33} (%)	kp (%)	kt (%)	Qm	f_{33}'/f_0
1	0	32.3	19.0	37.2	243	285
2	0.05	32.7	21.4	38.2	352	406
3	0.1	34.1	23.4	40.3	413	513
4	0.15	37.2	28.0	41.1	472	602
5	0.2	37.1	26.5	40.5	461	541
6	0.25	36.0	24.1	40.3	432	462
7	0.3	35.6	21.8	38.2	418	395
8	0.35	17.2	9.8	18.3	287	276
9	0.4	-	-	-	-	243

[0012] According to Table 1, it turns out that maximum 472 is obtained by X= 0.15 and Qm has improved Qm to TiO (Bi0.5Na0.5)3. However, in the range of X= 0 and 3<X, Qm is very as small as 300 or less, and it turns out that utilization is difficult.

[0013] Moreover, by 3<X, it is falling from drawing 1 rapidly to k33, kp, and kt not decreasing in 0< X<=0.3. Therefore, the range of 0< X<=0.3 is considered to be suitable for practical use.

[0014] As mentioned above, without degrading k33, kp, and kt of TiO(Bi0.5Na0.5) 3 by making LaFeO3 dissolve to 30-mol% to TiO (Bi0.5Na0.5)3, Qm can be raised and this becomes applicable to the use of a filter, vibrator, etc.

[0015]

[Effect of the Invention] As explained above, according to this invention, the piezoelectric-ceramics constituent which has a unleaded and high mechanical quality factor was able to be offered.

[Translation done.]